

CLAIMS

1. A method for preparing carbon nanotubes or nitrogen-doped carbon nanotubes by pyrolysis, in a reaction chamber, of a liquid containing at least one liquid hydrocarbon precursor of carbon or at least one liquid compound precursor of carbon and nitrogen consisting of carbon atoms, nitrogen atoms and optionally hydrogen atoms and/or atoms of other chemical elements such as oxygen, and optionally at least one metal compound precursor of a catalyst metal, in which said liquid is formed under pressure into finely divided liquid particles, such as droplets, by a specific injection system, preferably a periodic injection system, and the finely divided particles, such as droplets, formed in this way, are conveyed by a carrier gas stream and introduced into the reaction chamber, where the deposition and growth of the carbon nanotubes or nitrogen-doped carbon nanotubes take place.
2. The method as claimed in claim 1, in which said specific injection system is of the continuous or periodic automobile heat engine injector type.
3. The method as claimed in claim 2, in which the injection system is provided with a needle-type valve.
4. The method as claimed in claim 1, in which the nanotubes are regularly disposed or arranged in space, are generally aligned with respect to one another and are substantially perpendicular to the wall of the reaction chamber.
5. The method as claimed in any one of claims 1 to 4, in which the nanotubes have a length of from a few

micrometers, for example 1 to 10  $\mu\text{m}$ , up to a few millimeters, for example 1 to 10 mm.

6. The method as claimed in claim 1, in which said liquid hydrocarbon is selected from nonaromatic liquid hydrocarbons.

7. The method as claimed in claim 6, in which said liquid hydrocarbon is selected from C5 to C20 alkanes such as n-pentane, isopentane, hexane, heptane and octane; C5 to C20 liquid alkenes; C4 to C20 liquid alkynes; and C5 to C15 cycloalkanes such as cyclohexane.

8. The method as claimed in any one of claims 1 to 5, in which said liquid hydrocarbon is selected from optionally substituted C6 to C12 aromatic hydrocarbons such as benzene, toluene and xylene.

9. The method as claimed in any one of claims 1 to 5, in which said liquid compound consisting of carbon atoms, nitrogen atoms and optionally hydrogen atoms and/or atoms of other chemical elements such as oxygen is selected from liquid amines, for example benzylamine, or nitriles such as acetonitrile.

10. The method as claimed in any one of claims 1 to 9, in which said liquid is in the form of a solution of the metal compound precursor(s) of a catalyst metal in the liquid hydrocarbons(s) or in the liquid compound(s) consisting of carbon atoms, nitrogen atoms and optionally hydrogen atoms and/or atoms of other chemical elements such as oxygen.

11. The method as claimed in claim 10, in which said metal compound precursor of a catalyst metal is selected from the compounds consisting of carbon,

hydrogen, optionally nitrogen and/or oxygen and at least one metal.

12. The method as claimed in any one of claims 1 to 11, in which said metal compound precursor of a catalyst metal is selected from metal salts and organometallic compounds, such as metallocenes.

13. The method as claimed in claim 12, in which said metal salts are selected from metal salts in which the counterion of the metal consists of a heteroatom such as a halide.

14. The method as claimed in claim 12, in which said metal salts are selected from metal nitrates, acetates, acetylacetones and phthalocyanines, such as iron phthalocyanine and nickel phthalocyanine.

15. 15. The method as claimed in any one of claims 11 to 14, in which said metal is selected from iron, cobalt, nickel, ruthenium, palladium and platinum.

16. The method as claimed in either one of claims 12 and 15, in which said organometallic compound is selected from ferrocene, nickelocene, cobaltocene and ruthenocene.

17. The method as claimed in any one of claims 11 to 16, in which the solution also contains one or more compound(s) promoting the growth of the carbon nanotubes or nitrogen-doped carbon nanotubes, such as thiophene or precursors, for example nitrates or alkoxides, of rare earths such as yttrium, lanthanum and cerium.

18. The method as claimed in any one of claims 11 to 17, in which the concentration of the metal compound

precursor of a catalyst metal in the solution is generally from 0.2 to 15% by mass.

19. The method as claimed in any one of claims 11 to 18, in which the solution is a 2.5% by mass solution 5 of ferrocene, preferably in toluene and/or cyclohexane.

20. The method as claimed in any one of claims 1 to 9, in which said liquid is in the form of a colloidal suspension of metal nanoparticles in said at least one liquid hydrocarbon or in said at least one liquid 10 compound consisting of carbon atoms, nitrogen atoms and optionally hydrogen atoms and/or atoms of other chemical elements such as oxygen.

21. The method as claimed in claim 20, in which said metal nanoparticles are selected from 15 nanoparticles of iron, nickel, cobalt, ruthenium, palladium, platinum and of their mixtures or their alloys.

22. The method as claimed in either one of claims 20 and 21, in which one or more metal compound 20 precursor(s) of a catalyst metal, as described in any one of claims 10 to 16, is (are) also dissolved in said colloidal suspension.

23. The method as claimed in any one of claims 1 to 22, in which said finely divided liquid particles such 25 as droplets have a dimension, for example a diameter, of from a few tenths of micrometers to a few tens of micrometers, preferably from 0.1 to 20 micrometers.

24. The method as claimed in any one of claims 1 to 23, in which said specific injection system is periodic 30 and operates in pulses.

25. The method as claimed in claim 24, in which the number of pulses is from 0.96 to 1200 per minute.
26. The method as claimed in either one of claims 24 and 25, in which the volume of liquid injected in 5 each pulse is from 2 to 100 microliters.
27. The method as claimed in any one of claims 1 to 26, in which the finely divided liquid particles such as droplets formed by the injection system are evaporated in an evaporation device before they are 10 introduced into the reaction chamber.
28. The method as claimed in any one of claims 1 to 27, in which the pyrolysis is carried out at a temperature of from 600 to 1100°C, preferably from 800 to 1000°C, more preferably from 800 to 900°C.
- 15 29. The method as claimed in any one of claims 1 to 28, in which the pyrolysis is carried out for a time of from 5 to 60 min, preferably from 15 to 30 minutes.
30. The method as claimed in any one of claims 1 to 29, in which the pressure in the reaction chamber is a 20 controlled pressure, for example less than atmospheric pressure.
31. The method as claimed in any one of claims 1 to 30, in which the liquid contains a metal compound precursor of a catalyst metal, and the deposition and 25 growth of the nanotubes take place directly on the walls of the reaction chamber.
32. The method as claimed in any one of claims 1 to 30, in which the deposition and growth of the nanotubes take place on a substrate placed inside the reaction 30 chamber.

33. The method as claimed in claim 32, in which the liquid does not contain a metal compound precursor of a catalyst metal, and the substrate is provided with a catalyst deposit.
- 5 34. The method as claimed in claim 32, in which the liquid contains one or more metal compound precursor(s) of a catalyst metal, and the substrate may or may not be provided with a catalyst deposit.
- 10 35. The method as claimed in claim 32, in which the substrate is selected from quartz substrates, silicon substrates and substrates made of metal oxides such as Al<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, MgO and ZrO<sub>2</sub>.
- 15 36. The method as claimed in claim 32, in which the substrate is a fabric of carbon fibers or nitrogen-doped carbon fibers.
37. The method as claimed in claim 33 or 34, in which the catalyst deposit comprises one or more metals selected from transition metals such as Fe, Ni and Co, and other metals such as Pd, Ru and Pt.
- 20 38. The method as claimed in any one of claims 33, 34 and 37, in which the catalyst deposit is in the form of a thin film.
39. The method as claimed in any one of claims 33, 34 and 37, in which the catalyst is deposited discontinuously.
- 25 40. The method as claimed in claim 39, in which the catalyst deposit is in the form of a set of discrete entities, for example drops, beads, spots or dots of catalyst.
- 30 41. The method as claimed in claim 40, in which the deposit is ordered and said discrete entities are

arranged in the form of a network or pattern, for example a network of interconnected lines or rows.

42. The method as claimed in claim 32, in which the substrate consists of a layer of nanotubes or a 5 plurality of stacked layers of nanotubes.

43. A device for carrying out the method as claimed in any one of claims 1 to 42, comprising:

- a reaction chamber in which carbon nanotubes or nitrogen-doped carbon nanotubes are prepared by 10 pyrolysis of a liquid containing at least one liquid hydrocarbon precursor of carbon or at least one liquid compound precursor of carbon and nitrogen consisting of carbon atoms, nitrogen atoms and optionally hydrogen atoms and/or atoms of other chemical elements such as 15 oxygen, and optionally at least one metal compound precursor of a catalyst metal;
- means for forming said liquid under pressure into finely divided liquid particles such as droplets, for conveying said finely divided particles such as 20 droplets by a carrier gas stream and introducing them into the reaction chamber;
- in which device said means for forming said liquid into finely divided liquid particles, for conveying them and introducing them into the reaction chamber 25 comprise a specific injection system, preferably a periodic injection system, provided with an injection head, and a connection ring, in which the carrier gas intake is provided, connecting the injection system to the reaction chamber optionally via an evaporation 30 device.

44. The device as claimed in claim 43, in which the side wall of the connection ring includes at least one carrier gas intake tube, said carrier gas intake tube opening into an annular groove surrounding the 5 injection head of the system for injecting the liquid particles, and is placed behind it in order to surround the finely divided liquid particles without interfering with them.